XXVII.—*Notice of Further Experiments as to the Reduction of Metallic Oxides by the Peroxide of Barium.*

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The following experiments were made in continuation of an inquiry relating to the laws of the formation of the elemental bodies, which appeared some time since in the "Transactions of the Royal Society." To render them intelligible, I may briefly recall the general results of that investigation.

It was known from the experiments of Thénard, that when the peroxide of hydrogen is placed in contact with certain metallic oxides, both substances are decomposed. This decomposition, which was not in harmony with prevalent ideas as to the nature of chemical decompositions, had received the occasional attention of chemists, but never been made the subject of experiment. It occurred to me that this event was a chemical change of a peculiar kind, in which two particles of oxygen fulfilled the same function and produced the same results as in ordinary decompositions were produced by the particles of two elements,—as, for example, of oxygen and hydrogen,—and that the reduction which took place was due to the chemical combination of the oxygen from the peroxide of barium with the oxygen from the reduced oxide. From this point of view, I made experiments as to the ratio in which the oxygen was evolved from the two substances. These experiments, while they confirmed these views, have opened out a new and further field of research. Experiment showed that the loss of oxygen from the reduced oxide bore a definite, but yet a variable, ratio to the loss from the peroxide of barium; that in all cases this ratio was comprised between two limits; the amount of reduction might be almost indefinitely diminished, in which case the action of the metallic oxide approached to that action of platinum or carbon which goes by the name of catalysis; and that, by changing the circumstances, the amount of reduction might be so increased as to approach very closely to a loss of equal equivalents of oxygen from the two substances. This loss of equal equivalents was realised in the case of the action of a mixture of iodine and water upon peroxide of barium, in which experiment water itself may be regarded as the oxide reduced. The ratios intermediate between these limits indicated a remarkable law. This ratio varied with several circumstances,—with the nature of the chemical substance reduced, with the temperature, and with the mass. It appeared that when the relative proportion of the

substances was varied, other circumstances being the same, this ratio changed, not continuously, but by intermittent steps; so that while at certain points there appeared to be a continuous increase of loss, as the quantity of the metallic oxide was increased, at certain other points, this quantity might be very greatly varied without any alteration of the ratio. Since these experiments, the existence of this law in other cases of the action of mass has been placed beyond a doubt by the researches of Bunsen and of Debus.

The method by which my experiments were conducted was not sufficiently exact to bring out these numerical results with the accuracy desirable, and I turned my attention to other modes of effecting this object. The plan I have adopted is that of acting upon weighed quantities of the peroxide of barium with solutions of metallic salts of known strength.

I have thrown into the annexed table the result of some of these experiments, which were made with solutions of nitrate of silver. The oxygen was measured by the amount of silver reduced, which was determined as chloride. The ordinates measure this loss of oxygen, the oxygen in the peroxide being estimated at 100. In the series marked A and B, the temperature was varied, while the strength of the silver solution was the same, the quantity of which taken corresponded to two equivalents in relation to the oxygen in the peroxide. The variations of temperature are indicated by the abscissa. Different preparations of the peroxide of barium were used in the two series of experiments. In series A, assuming the oxygen in the peroxide as 100, the oxygen corresponding to the silver reduced at the temperatures 100° , 75° , 70° , 65° , 60° , 55° , 50° , 40° , 30° , 7° , 0° , was 39, 39, 40, 42, 45, 47, 50, 52, 52, 55, 65. In series B, the oxygen corresponding to the silver reduced at the temperature 100° , 70° , 65° , 40° , 30° , 8° , was 43, 44, 48, 60, 60, 67.

It will be perceived that in each of these series of experiments there are two intervals of constant action. These intervals lie, in both cases, between 100° and 75° , and between 40° and 30° . The exact length and position of these intervals, the experiments are not sufficiently numerous to determine. This indicates the existence of a law, in the case of temperature, analogous to the law of mass.

The dotted lines give the result of three series of experiments, in which the temperature and the strength of the solution were constant, but the quantity of the solution employed was varied. The abscissa in this case gives the amount of the solution taken, as measured by the oxygen equivalent to the amount of silver contained in it. Thus where the numbers 50, 100, 150, appear in the lower line, the solution employed contained $\frac{1}{2}$ an equivalent, 1 equivalent, and $1\frac{1}{2}$ equivalents of oxygen, relative to the amount of oxygen in the peroxide of barium. The experiments indicated by the line *c* were made at 100° C. The loss of oxygen corresponding to the quantities 50, 100, 150, 200, 300, and 400, were 50, 50, 52, 53.5, 53.5, 53.5. Here again appear two constant intervals of action, namely where the variation was from $\frac{1}{2}$ to 1 equivalent, and from 2 to 4 equivalents.

The line *d* relates to experiments made with the same preparation of peroxide as in *c*, and with the same solution, but at a temperature of 14° to 15° C. The loss of oxygen, as given by experiment, corresponding to the quantities of solution indicated by the numbers 50, 100, 150, 200, 250, 300, 350, 400, 500, and 600, was 46.6, 68.2, 73.4, 73.6, 72.8, 72.7, 72.3, 71.6, 72.0, 71.5. The mean of the last eight experiments gives 72.7, which is the number given in the table. The experiments were made at the temperature of the air. The experiments 1, 2, 3, 4, were made at one time, the experiments 5, 6, 7, 8, 9, 10, at another. The slight variation which these latter numbers present is probably due to an alteration of temperature. In this case the action is constant after the quantity has been increased beyond $1\frac{1}{2}$ equivalents.

The experiments *e* were made at a temperature of about 8° C., with the same preparation of peroxide as in the last series, but with a solution containing half the quantity of nitrate of silver, compared with the solutions used in the two preceding series. The amount of oxygen lost corresponding to the quantities 50, 100, 150, 200, 250, 300, 350, 400, was 48, 53, 65, 67, 68, 69, 70, 70. In this case the maximum action was reached when $3\frac{1}{2}$ equivalents of the solution were employed.

There is yet a third variable besides temperature and absolute mass, which, from the very nature of the experiment, it is not possible

to render constant. The action varies, not only with the absolute quantity of the silver solution employed, but also with the strength of that solution. Now the amount of silver in the solution, from the very decomposition which takes place, must change at every moment of the experiment. This variation has, doubtless, an important influence on the result; and although it cannot be entirely eliminated, yet it is obvious that, in the case of large quantities of the solution, the relative alteration of the solution is much less than with small quantities, and it is probable, that after that point where the action becomes constant, this effect is so small as not to be perceptible. The variations exhibited in the above experiments are with some substances much greater than with others, and in certain cases do not exist. For example, a solution of chloride of gold gave almost the very same amount of reduced gold, whether the experiment was made at 100° , or at the temperature of the air, and whether the solution were concentrated, or diluted with many times its bulk of water. The reduced gold corresponded to a loss of about 80 parts of oxygen from the solution to 100 from the peroxide.

In a recent number of Liebig's *Annalen*, Professor Wöhler, who does not seem to be aware, either of the theoretical views which have been put forward, or of the experiments which have already been made upon this subject, states that when a solution of peroxide of hydrogen in hydrochloric acid is acted upon by peroxide of manganese, that the oxygen evolved is exactly twice the oxygen due to the decomposition of the peroxide of hydrogen alone. The probable cause of the deviation which, in any case, appears from this result, is the simultaneous decomposition of the peroxide of hydrogen by two operations which, in the present state of our knowledge, we must regard as distinct,—namely, by the chemical action of the metallic oxide, and by that action which is termed catalytic, and which is produced either by the oxide itself or by the reduced metal which is formed. On the nature of this so-called catalytic action, or on the propriety of this term, I am passing no opinion, but am simply referring to a fact. In the experiment with iodine, above alluded to, this latter operation is entirely eliminated, and it is possible that, in the form of Professor Wöhler's experiment, the same result may be obtained. In the numerous experiments, however, which I have myself made upon this subject, I have not absolutely attained this result, except in the single instance referred to. By acting upon a mixture of peroxide of lead and peroxide of barium with dilute acetic acid, I have obtained a loss of 90 parts of oxygen from the peroxide of lead, and with peroxide of nickel,

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in one experiment, a yet greater loss; but in every experiment with similar substances there was a certain deficiency. An interesting case of the reduction of peroxide of manganese is afforded by the mineral pyrolusite. In four experiments with this substance, made with dilute acetic acid, in which one equivalent of peroxide of barium was taken respectively to 4, 2, 1, and 1 equivalents of the pyrolusite, the loss of oxygen from the pyrolusite, to 100 parts of oxygen in the peroxide of barium, was 49·8, 48·9, 49·1, 50·9. The amount of reduction, on the other hand, exhibited by the mineral braunite, was very trifling: the action of this substance was nearly the same as that of platinum.